EMJ MS
EUROPEAN MULTIDISCIPLINARY JOURNAL OF MODERN SCIENCE
https://emjms.academicjournal.io/index.php/ Volume:6

Synthesis of Vinyl Ether Wine Acid and Application of Synthes Products in Agriculture

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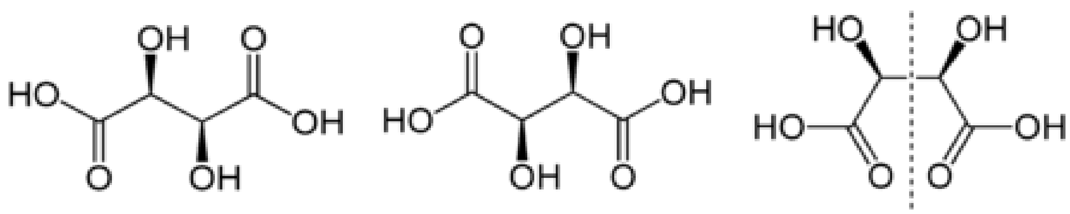
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Annotation: This article describes the synthesis of mono- and divinyl esters from dibasic carboxylic acids, including wine acids, in a homogeneous solution of dimethylformamide (DMF) in the presence of zinc acetate and $AlCl_3 \cdot 6H_2O$ catalysts.

Keywords: wine acid, dimethyl formamide (DMFA), zinc acetate, catalyst, vinyl reaction, fungicide, rust disease.

Wine acid is a common natural compound. It is found in significant amounts in the sour juices of many fruits, such as grape juice. D-grape acid is obtained by the action of mineral acids on the acidic potassium salt (tartar) formed during the fermentation of grape juice.

Three stereoisomeric forms of tartaric acid are known: D - (-) - enantiomer (a), L - (+) - enantiomer (b) and meso-form (c) (mesowine acid):

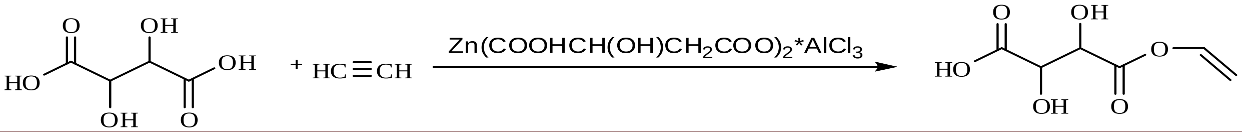


a б c

The reactions of tartaric acid with acetylene were studied. The DMFA-catalyst system was used in this reaction. The DMFA-catalyst system is a catalytic system prepared by dissolving the salt $Zn(CH_3COO)_2$ as a catalyst in a dimethylformamide solvent medium and as a 10% $AlCl_3$ socatalyst relative to the mass of zinc acetate.

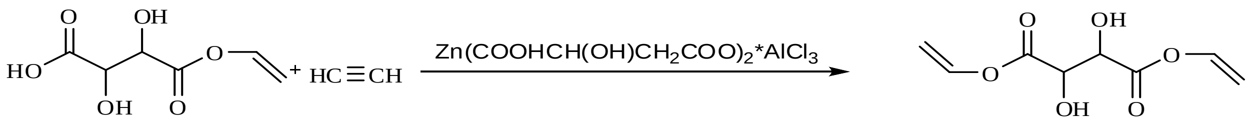
Let us consider the mechanism of the vinyl reaction in the example of tartaric acid:

1-scheme



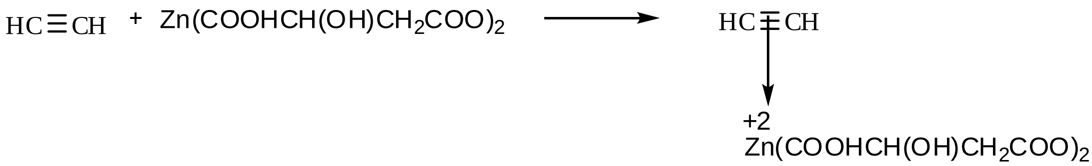
The monovinyl ether formed by the acid reacts with acetylene in the presence of a catalyst to form divinyl ether.

2-scheme



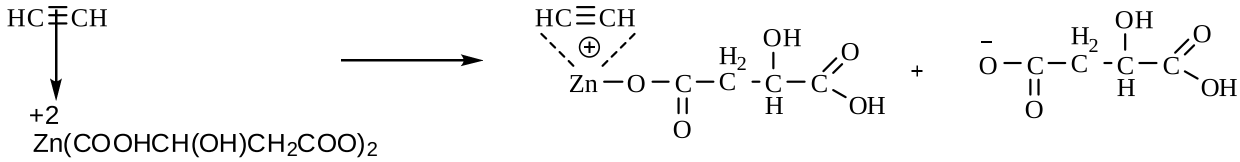
The reaction mechanism is as follows. Initially, the zinc acetate catalyst reacts with acetylene in a DMFA medium to form a π -complex.

3-scheme



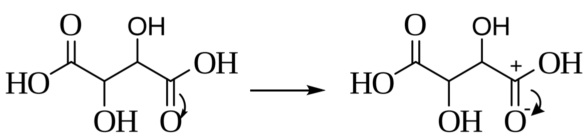
A single p-bond of acetylene is broken from the resulting p-complex to separate the δ complex and the acetic acid anion.

4-scheme



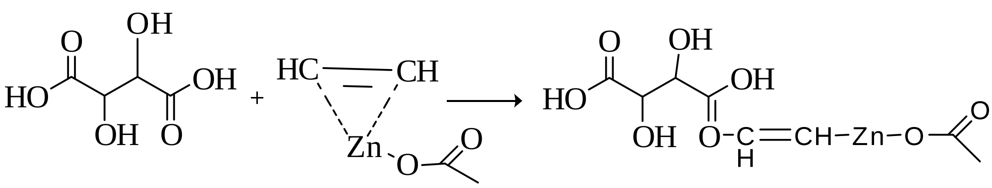
Due to the high negative charge value in oxygen in the carbonyl group of tartaric acid, oxygen is partially negatively charged in the solvent environment.

5-scheme



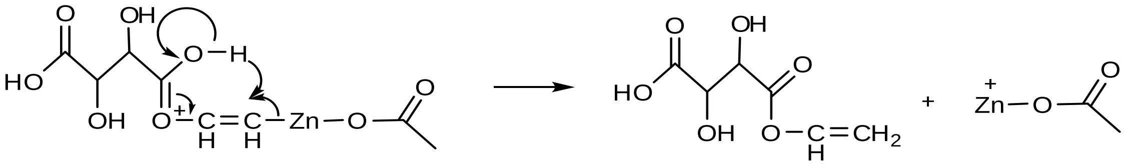
The cation of vinyl acetorux interacts with the acid anion to form a complex.

6-scheme



The resulting acetic acid compound of the monovinyl ester of tartaric acid undergoes β-elimination to form the monovinyl ester of dioxyacarboxylic acid.

7-scheme



In the same order, the second and third carboxyl groups are vinylized to form divinyl and trivinyl esters of dioxyacarboxylic acid. The process takes place, of course, through the formation of acetorux complexes of monovinyl acid and acetorux complexes of divinyl acid.

The synthesized vinyl esters are named as follows:

1. WA MVE –Wine acid monovinyl ether.
2. WA DVE – Wine acid divinyl ether.

The test was conducted on a field planted with "Krasnodar" winter wheat to determine the effect of new drugs against yellow rust. The fields designated for the test were chemically treated 3 times (on 25.03, 03.04 and 10.04) with a 0.005% working solution of the drugs using a motor sprayer during the spinning and spinning phases of wheat.

The first treatment was carried out at the initial appearance of the disease and 7–10 days before the onset of high temperature, during the transition of the fungi to the stage of conservation (teliostadia). The degree of damage to plants was assessed using the Peterson et al scale, as well as guidelines for fungicide registration tests in agriculture. Biological efficiency is calculated as a percentage using the Ebot formula:

$$A = \frac{K - B}{K} \times 100$$

Here: A - biological efficiency,%;

K - is the final level of crop damage in the controlled area (uncultivated area);

B- is the final level of crop damage in the experimental area.

As a result of the test, the drugs used (WA MVE, WA DVE) were observed to be effective in combating yellow rust (shown in the table).

Table. Dynamics of development of yellow rust disease in "Krasnodar" wheat and biological effectiveness of fungicides

№	Experiment options	Repeatability	Damage ratio on the set dates, %						
			25.03	3.04	Б.С, %	10.04	Б.С, %	17.04	Б.С, %
1	ВК МВЭ	3 times	1,0	0,5	84,4	1,5	88,1	0,8	90,2
2	ВК ДВЭ		1,0	0,6	80.6	1,8	82.4	1,0	85,6
3	Control (unprocessed)	–	1,0	3,2	–	8,2	–	12,6	–

Three applications of the drug allowed to achieve the highest results in relation to untreated areas. At the same time, the maximum level of damage to the crop area not treated with the drug was higher than 12.6, and when using the drug, the degree of damage was reduced to 0-0.8, or the disease was eliminated up to 90%.

These new compounds are recommended for extensive research as pesticides against yellow rust (Puccinia striiformis) in grain crops.

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